FORMS
AND VOLATILITIES
OF TRACE
AND MINOR ELEMENTS
IN COAL

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I A comparison
of three pyrolysis units

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II Feasibility of a graphite
trapping system

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ACKNOWLEDGMENTS

PART I. A COMPARISON OF THREE PYROLYSIS UNITS

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ABSTRACT

Three laboratory pyrolysis systems were used to measure the volatilities of
trace and minor elements in five coals during pyrolysis. Preliminary
results from studies of one low-sulfur and one high-sulfur Illinois coal
charred at 50°C intervals from 200-700°C indicate that the temperatures of
450°C and 600-700°C are appropriate for the study of element movement.

Chlorine, Br, and Se were lost from at least four of the five coals studied;
Pb was lost from three coals. Arsenic, Sb, Cu, I, Co, and U were only partly
volatilized from one or two of the coals. Chromium and Zn were occasionally
lost in trace concentrations, indicating their low mobilities.

The volatility of an element could not be predicted reliably from measures
of the element's organic association. An element's volatility during coal
pyrolysis depends not only upon the element's association or mode of
occurrence but also upon physical changes within the coal and upon chemical
reactions of the element with sulfur or other volatile species. Mobility
may be either enhanced or inhibited depending upon whether the newly-formed
compound has a higher or lower volatility than the original compound in the
coal.

A new method of measuring element mobility during pyrolysis of coal (the
graphite trap method) is described. When the coal is heated the mobile
elements move from the coal to form intercalated compounds with graphite or
alternately are sorbed by it; the graphite is subsequently separated from
the coal and analyzed. Preliminary results for Illinois No. 5 and No. 6
coals indicate that the graphite trap method measures element mobility much
more sensitively than do the three other methods. As many as 26 elements
were identified in one of the graphite traps.

INTRODUCTION

The study of inorganic species formed during coal combustion has application
to environmental and economic aspects of increased coal utilization.
Greater use of coal for electric power generation will require a better
understanding of the release of inorganic species from coal, especially the
potentially hazardous elements. Liquefaction and gasification will play a
new role in coal utilization. Investigation of the behavior of an element
at intermediate temperatures (300-700°C) can yield information on its effect
on the catalysts used in such processes. Also, certain elements in coal
have catalytic properties themselves which may influence the type or amount
of product produced.

The association or combination in which an element occurs in coal will influence--if not control--its reactivity or volatility. One indirect method of estimating whether an element is associated primarily with the mineral fraction of coal or with its organic fraction is by the analysis of fractions of coal separated by specific gravity differences. Gluskoter et al. (1977), when using mine coals, demonstrated that this technique could be used to calculate an organic affinity index. The calculated organic affinity index was proposed as a way of comparing trace element associations within a given coal sample.

An alternative method of determining the association of elements is by the selective digestion of coal with acids (Kuhn et al., 1980). This chemical dissolution procedure was thought to leave a relatively unaltered organic coal "molecule" or fraction while removing virtually all of the inorganic mineral portion of the coal. Evidence supporting this conclusion was the lack of a detectable decrease in the organic sulfur content of the mineral-matter-free coal. Kuhn et al. (1980) concluded that extrapolation of the concentrations of trace elements in float/sink data to zero mineral matter content was comparable to results of acid extractions. Study results also indicated that most elements were associated primarily with the inorganic or mineral fraction of coal.

Other studies have investigated the fate of trace elements in coal-fired electrical power plants. Most studies involved an attempt to conduct a mass balance for a large suite of elements during the combustion process. However, results of such investigations are often difficult to compare because different types of coals were burned and different operating conditions existed in the power plants studied.

Klein et al. (1975) conducted a mass balance of 37 trace elements in which elements were classified according to their partitioning among the slag, fly ash, and vapor phase in the power plant studied. Twenty elements were not volatilized and remained in the slag. Arsenic, Cd, Cu, Ga, Pb, Sb, Se, Mo, and Zn were thought to be partly volatile and incorporated into the fly ash. Mercury, Cl, and Br were found to be almost totally lost to the vapor phase. Andren et al. (1975), reporting further on the Se mass balance, found that 68 percent of the Se was incorporated into the fly ash and 32 percent was vaporized.

Davidson et al. (1974) measured the concentration of 25 elements as a function of the particle size of the fly ash. They proposed that elements with higher volatility (Pb, Tl, Sb, Cd, Se, As, Ni, Cr, and Zn) would be preferentially concentrated on small particles. It was observed that these elements formed compounds with boiling points below the temperature of the combustion zone (1300-1600°C).

Kaakinen et al. (1975) measured the concentrations of 17 elements in a study of mass balance of a western coal-fired power plant. On the basis of these reported concentrations, elements were classified into two groups, with Pb, Cu, Sb, Zn, As, Mo, Hg, and Se in the volatile or partly volatile group.

Coles et al. (1979) measured the concentration of 42 elements in four size fractions of ash from a large western coal-fired power plant. They proposed a grouping of elements (similar to Kaakinen's) on the basis of their

particle-size dependency. Arsenic, Cd, Ga, Mo, Pb, Sb, Se, W, and Zn, found to be the most volatile, were associated with small particles. Barium, Be, Co, Cr, Cu, Ni, Sr, U, and V were found to be associated with intermediate particle sizes and were thought to be partly volatilized.

Roy et al. (1981) reviewed the literature on the environmental impact of coal fly ash. Arsenic, B, Br, Cl, Hg, I, In, Pb, Po, S, Sb, Se, and Zn were frequently reported as being concentrated in fly ash relative to the ash of parent coals. A volatilization-surface condensation mechanism was thought to account for this partitioning of elements.

Bertine and Goldberg (1971) used emission data from direct current arc spectrometers to develop an order of volatility: for combined elements occurring as volatile oxides, sulfates, carbonates, silicates, and phosphates, the order is As, Hg>Cd>Pb, Bi, Tl>In, Ag, Zn>Cu, Ga>Sn>Li, Na, K, Rb, and Sc; for uncombined elements the order is Hg>As>Cd>Zn>Sb⩾Bi>Tl>Mn>Ag, Sn, Cu>In, Ga, and Ge; for the sulfides the order is As, Hg>Sn, Ge⩾Cd>Sb, Pb>Bi>Zn, Tl>In>Cu>Fe, Co, Ni, Mn, and Ag. They expected a transfer of As, Hg, Cd, Sn, Sb, Pb, Zn, Tl, Ag, and Bi to the atmosphere during fuel combustion.

Block and Dams (1975) studied the distribution of 44 elements in Belgian coals and in the ash produced at 900°C in the laboratory. They found that under the conditions of the experiment only the halogens Se and Hg were lost because of volatilization and that Sb and As were only partly lost.

Ting and Manahan (1979) studied the volatilities of eight trace elements in an untreated coal and in a coal spiked with inorganic and organic forms of the elements. Pyrolysis temperatures up to 1000°C were used. Results from the untreated coal indicated that 68 percent of the Br, 95 percent of the Cl, 53 percent of the Se, and 50 percent of the As were volatile while V, Mn, Cr, and Co were retained in the char. Selenium and As were considerably less volatile in the coal samples spiked with organic forms of Se and As than in coal samples spiked with inorganic forms of Se and As. This suggests that these two elements in this particular coal occur in both inorganic and organic association.

Lee, Johnson, and Fisher (1977, 1980) studied the volatility of 15 elements in an Illinois Herrin No. 6 coal (first ashed at 340°C) in the temperature range of 540-1250°C under dry and humidified oxidizing conditions. Zinc, Mn, Ni, Co, Cu, Cr, Li, and V were completely retained in the ash. Chlorine was the only element that showed a high loss; 98 percent of the chlorine was lost during the 340°C ashing.

Ruch, Gluskoter, and Shimp (1974) reported the results of ashing coal in a muffle furnace at temperatures up to 850°C. They found that Zn, Cd, Ni, Mn, Co, Cr, Cu, Be, Pb, B, Ge, and Sn were retained in the ash, but that up to 25 percent of the V was lost. At low-temperature ashing conditions (no higher than 150°C) the elements Ga, Se, As, Zn, Ni, Co, Be, Cu, Pb, V, Mn, Cr, and Cd were retained; up to 90 percent of the Hg, 100 percent of the Br, and up to 50 percent of the Sb was lost.

Mitchell and Gluskoter (1976) studied the variation of mineralogy in coal as a function of temperature in the range of 400-1400°C. At temperatures up to 400°C most minerals remained unchanged, but at higher temperatures

transformations occurred to the point that the sample became completely fused into an amorphous glass. These results suggest that mineral transformations of major elements (and probably also of many trace elements), do not result in significant mobility of elemental species. Once the coal has been fused into a glass, any movement of elements not organically bound would be unlikely.

The purpose of this investigation was to evaluate the mobilities of up to 40 trace elements in various types of coals from different regions and to relate the form(s) of a trace element to the mobility of that element when coal is pyrolyzed. On the basis of our preliminary work two pyrolysis temperature ranges (400-450°C and 600-700°C) were chosen. Input coals and their resultant chars were analyzed to determine indirectly the amount of loss for each element. For a number of the coals studied the volatile fraction was trapped and analyzed in an attempt to obtain direct determinations. Three pyrolysis experimental designs were used; each had inherent advantages and disadvantages.

CONCLUSIONS AND RECOMMENDATIONS

A number of elements were volatile even at the relatively low temperatures used in this study, and each coal had unique properties that controlled the volatility of its elements. Prediction of volatility of an element on the basis of its organic or inorganic association is difficult and uncertain at best. The relationship of an element's volatility to the changing structure of coal as a function of temperature is of critical importance, but is not well understood.

Results of our preliminary studies indicate that it would be advantageous to continue these studies at higher temperatures to the point at which the coal's structure totally breaks down. Additional measurements on surface area or pore size changes at higher temperatures should also be made.

Further work needs to be done to evaluate the usefulness of graphite traps (described in the appendix), for studies of element mobility in coal.

EXPERIMENTAL PROCEDURES

Coals studied

Five Illinois coals, a lignite from N. Dakota, and a medium volatile coal from Alabama were used in this study. All coals were collected by Illinois State Geological Survey personnel by procedures outlined in Gluskoter et al. (1977). Table 1 lists the state, seam, rank, sample type and analysis number of the coals studied. Five of the seven coals chosen had been previously studied by Gluskoter et al. (1977) and Kuhn et al. (1980); these two studies provided useful information on the chemical association of the elements based on float-sink and/or acid-demineralization procedures. Although the samples represent the same mine they are not always splits of the same sample and variations due to sampling could exist. To insure consistency within each pyrolysis experiment, a split of the whole coal from which char was prepared was also analyzed.

TABLE 1. IDENTIFICATION OF WHOLE COALS STUDIED.

Analysis Number	State	Seam	Rank	Sample Type
C18185	Illinois	Springfield (No. 5)	HVCB	C
C18440*	N. Dakota	Ft. Union Formation	Lignite	FC
C18527	Illinois	Herrin (No. 6)	HVBB	CFC
C18571*	Illinois	Herrin (No. 6)	HVCB	FC
C18848*	Alabama	Blue Creek Seam	MVB	FC
C18857*	Illinois	Herrin (No. 6)	HVBB	FC
C17016*	Illinois	Herrin (No. 6)	HVCB	C
C21554#	Illinois	Springfield (No. 5)	HVAB	C
C21555#	Illinois	Springfield (No. 5)	HVCB	C
C21556#	Illinois	Herrin (No. 6)	HVCB	C

* Analysis number as appears in Gluskoter et al. (1977).
\# Used only for studies described in appendix.
  C = Channel; FC = Face Channel; CFC = Composite Face Channels.

Analytical procedures

Methods for chemical analyses used in this study--outlined in detail by Gluskoter et al. (1977) and Ruch et al. (1979)--include:

    X-RAY FLUORESCENCE (XRF): Al, Ca, Cl, Mg, Si, Ti, P
    INSTRUMENTAL NEUTRON ACTIVATION (INAA): Fe, K, Na, As, Br, Ce, Co, Cr,
        Cs, Eu, Ga, Hf, La, Lu, Mn, Ni, Rb, Sb, Sc, Se, Sm, Ta, Th, U, W, Yb, Zn
    ATOMIC ABSORPTION (AA): Cu, Pb, Ni
    ENERGY DISPERSIVE X-RAY FLUORESCENCE (XES): Ba, I, Sr
    AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM): Moisture, volatile
        matter, total sulfur

AA results were obtained for sample sets DK3 only; The ASTM method used was from the 1980 Annual Book of ASTM Standards, Part 26.

Surface area measurements were made by procedures given in Thomas and Damberger (1976).

A single method of analysis was used for an element throughout a given pyrolysis experiment to insure data consistency. For a number of elements, instrumental neutron activation (INAA) rather than X-ray fluorescence (XRF) was used because the former method had better sensitivity for the analysis of trapped volatile fractions.

Pyrolysis units

Three experimental coal pyrolysis units were used in this work, and a number of adaptations and design changes were made in the units during the course of the investigation. The results discussed in this paper represent results obtained during optimum operating conditions for each individual unit.

Results from the pyrolysis unit that used the smallest amount of starting coal (approximately 10 grams) are designated as DK1, DK2, and DK3 in the results section. Figure 1 is a schematic representation of this quartz

retort experimental unit. Coals were pyrolyzed in an inert atmosphere
by maintaining a flow of about 100 cm^3/min of nitrogen gas. Coals were
dried at 110°C prior to each experiment and a split of the same sample
was saved for elemental analysis.

The second pyrolysis apparatus, the Parr Pressure Reaction Apparatus
(RHS), had a larger capacity, normally about 100 grams (fig. 2). All
coals were dried at 177°C before each run to eliminate as much water as
possible. Oils, tars, and gases were swept from the reaction apparatus with
nitrogen (∿200 cm^3/min) and collected in a baffled trap containing a 50:50
mixture of tetrahydrofuran and dimethoxypropane at -30°C. The dimethoxy-
propane was used to scavenge the water produced during coking and to assure
a dry sample after evaporation. The condensed tar was analyzed for
volatilized elements.

The third apparatus (designated as CK) was a continuous-feed char-
ring oven that required about 1.5 kg of coal for each test. Additional
coal was fed into the oven before and after the measured charge to assure
uniform conditions throughout the test. Figure 3 is a schematic representa-
tion of this unit. Details of the construction and operating parameters of
this furnace are given in Kruse and Shimp (1981). Coals used in this unit
were splits of the same samples used in the Parr Pressure Reaction Apparatus
(RHS). This unit differed from the first two in that no attempt was made
to trap volatiles and the nitrogen atmosphere used in the previous two
units was replaced by an atmosphere of the volatilized products. In the
first two batch units, the coal was brought up to the desired temperature
slowly; however, in the continuous-feed unit a thin bed of coal (3-5 mm in
depth) was used and the residence time in the oven was relatively short.

The temperature reported was that at the oven exit. The volatilized
water and the components with low boiling points kept the inlet
temperature 100 to 200°C lower than the exit temperature. The removal of
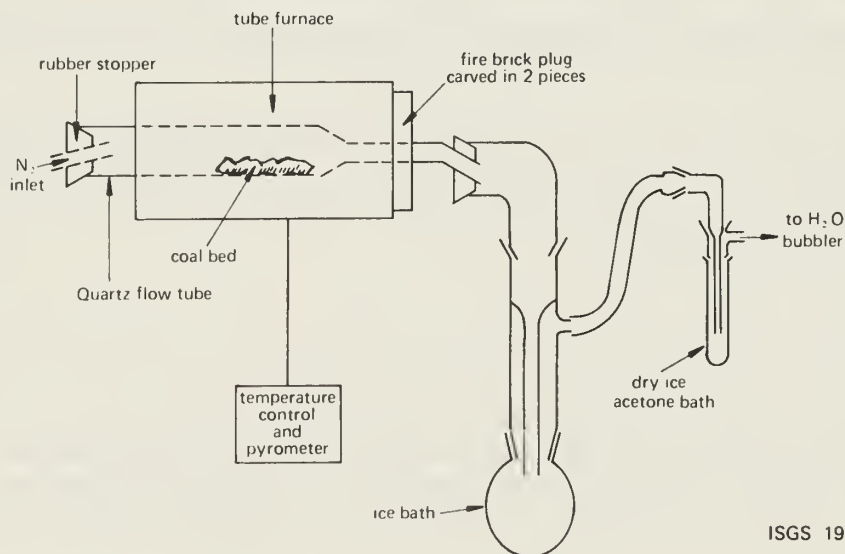
FIGURE 1. Quartz retort (DK).
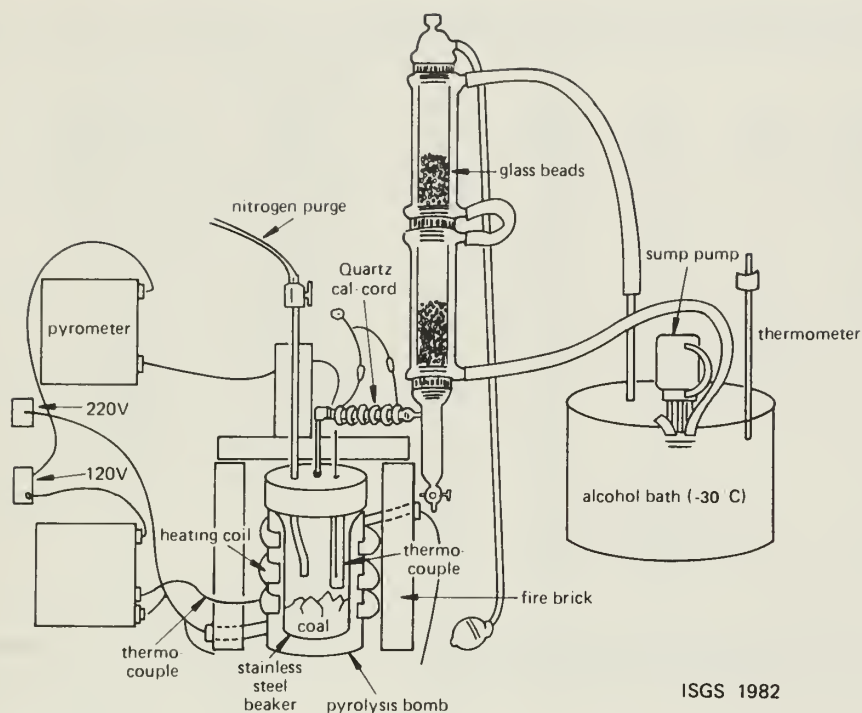
FIGURE 2. Modified Parr Pressure Reaction Unit (RHS).
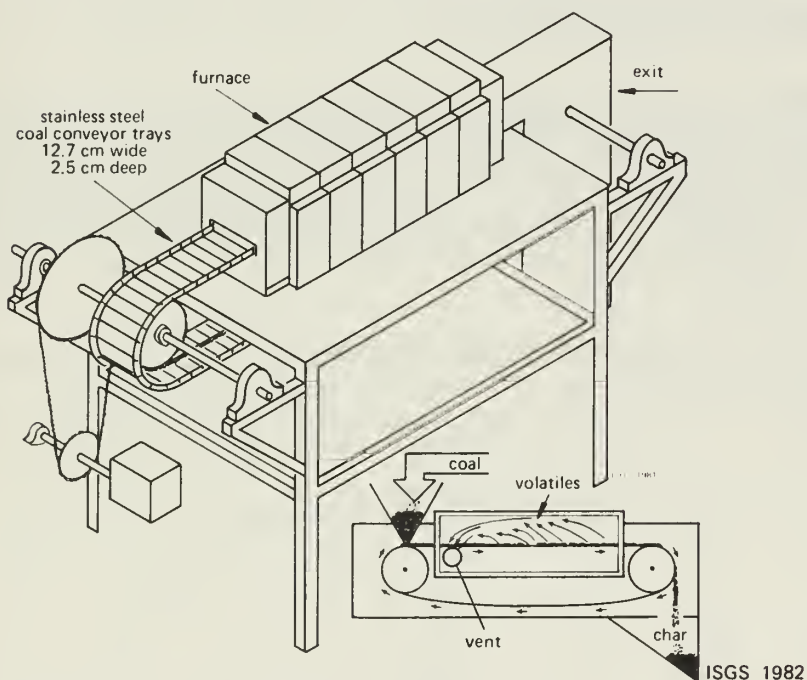
FIGURE 3. Continuous-feed charring furnace (CK).

volatile components was in a direction counter to the direction of coal movement; this counter movement provided a minimum exposure of the char at a given temperature to volatile components produced at a lower temperature. This configuration not only facilitated the removal of sulfur with the volatile matter but also produced char with a high internal surface area (as measured by adsorption of nitrogen gas).

TABLE 2. RESULTS OF CHARRING EXPERIMENT CONDUCTED AT 50°C INTERVALS (C17016 STARTING COAL).

Analysis Number	Temp (°C)	Time (hr)	Wt loss (%)	Surface area m^2/gr	Total sulfur (%)	As rec'd Volatile matter (%)	Volatile (%) (ash moisture free)	ISA m^2/g Charred
C19154	Raw Coal	--	--	241	4.22	36.4	42.0	241
C19155	177	6	3.5	259	4.00	33.6	38.1	250
C19156	250	22	4.7	270	3.94	32.4	36.5	257
C19157	300	24	8.0	285	4.03	27.4	31.4	262
C19158	350	24	13.5	281	3.38	23.8	27.2	243
C19159	400	24	23.8	295	2.45	17.0	19.9	225
C19160	450	24	24.8	316	2.21	13.1	15.3	238
C19161	500	24	28.2	323	2.39	8.2	9.6	232
C19162	550	20	30.4	321	2.19	7.4	8.7	223
C19163	600	20	29.6	345	2.36	6.9	8.2	246
C19165	650	20	30.9	352	2.14	4.6	5.5	243
C19166	700	20	28.5	372	2.32			

All samples dried at 177°C for 6 hours except C19154.
ISA = Internal surface area.

RESULTS

Selection of experimental charring temperatures

In the initial stages of this research a sample of high-sulfur Illinois No. 6 coal (C-17016) was extensively studied in the Parr Pressure Reaction Apparatus; changes were noted in volatile matter, sulfur content, and surface area over a temperature range of 177-700°C at approximately 50°C intervals. Results are shown in table 2; they are also plotted as temperature vs total sulfur (fig. 4), temperature vs percent volatile matter (fig. 5), and temperature vs surface area (fig. 6).

About half the sulfur is removed between 300-400°C (fig. 4) and the amount of volatile matter released (fig. 5) tends to level out near 500°C. The plot of temperature vs internal surface area (fig. 6) indicates an overall
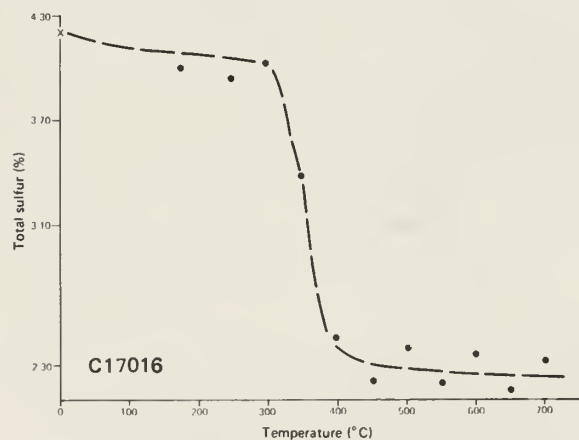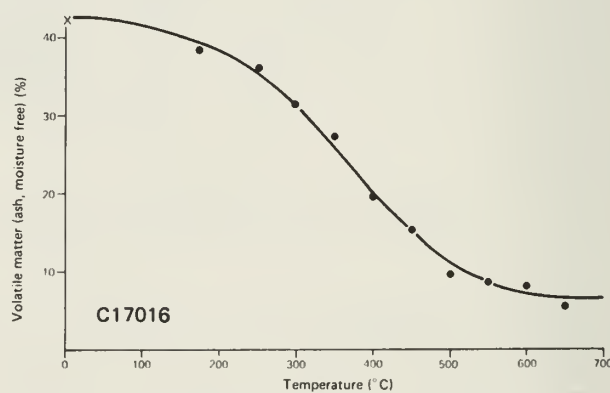

FIGURE 4. Temperature vs total sulfur.

FIGURE 5. Temperature vs percentage of volatile matter (ash, moisture free).

increase of internal surface area for residues of heat treatments from $100°$ to $700°$ C with a dip in the curve at about $360°$ C. This coal had a softening temperature of $379°$C, a fusion temperature of $390°$ C, and point of maximum fluidity of $417°$C. A similar dip in the curve has been observed for other coals; when the surface area is plotted against the surface area per gram of coal charged, the curves show another decline at about $650°$ C (Kruse and Shimp, 1981.

A second Illinois No. 6 coal (C18527) with low sulfur content was studied in a manner similar to that used with the high-sulfur coal (C17016). The

FIGURE 6. Temperature vs internal surface area.

analytical results for sulfur, volatile matter, surface area, and chlorine (table 3) are also plotted as temperature vs sulfur content (fig. 7), temperature vs chlorine (fig. 8), temperature vs percent volatile matter (fig. 9), and temperature vs surface area (fig. 10).

Comparison of temperature vs total sulfur results (fig. 7) for this low-sulfur coal (C18527) and the previous high-sulfur sample (fig. 4) shows a similar pattern: most of the sulfur loss occurs between $250-400°$C, and the loss of volatile matter is greatest between $300-500°$ C (fig. 9). Plots of internal surface area changes versus temperature, however, are some-

TABLE 3. RESULTS OF CHARRING EXPERIMENT CONDUCTED AT $50°$C INTERVALS (C18527 STARTING COAL).

Analysis Number	Temp. (°C)	Time (hr)	Wt Loss (%)	Surface Area m^2/gr	Internal Surface area m^2/g Charged	Total Sulfur	Chlorine	% Volatile (ash, moisture free)
C18675	Raw Coal	--	--	215	215	1.45	0.33	39.9
C18676	250	53	8.6	190	174	1.40	0.22	34.0
C18677	300	48	12.2	240	179	1.29	0.14	28.5
C18678	350	48	18.8	---	---	1.08	0.12	26.1
C18679	400	48	22.8	345	266	1.01	0.09	16.2
C18680	450	48	26.4	345	254	0.96	0.09	14.7
C18681	500	48	28.6	346	247	0.94	0.06	5.5
C18749	550	48	30.9	348	240	0.83	0.05	4.5
C18741	600	48	31.3	344	236	0.69	0.04	2.8
C18744	650	48	31.7	390	266	0.96	0.05	3.4

All samples dried at $177°$C for 6 hours.
ISA = Internal surface area

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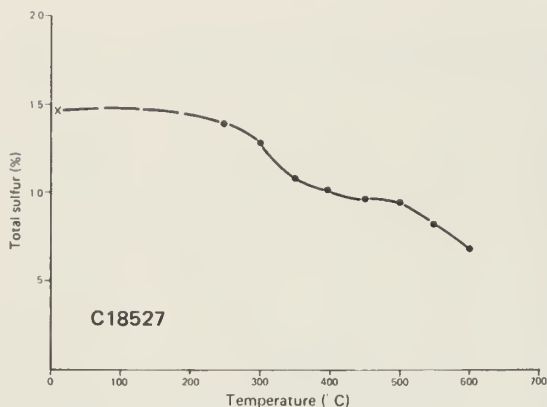
FIGURE 7. Temperature vs total sulfur.
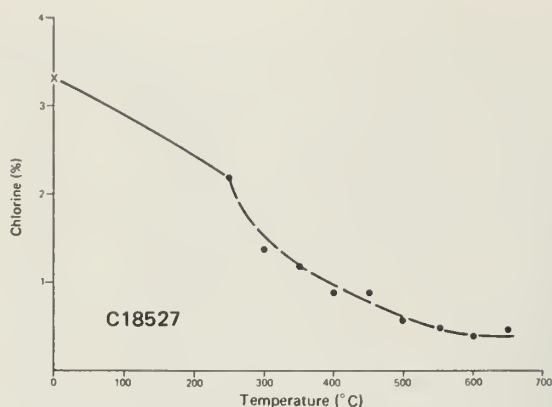
FIGURE 8. Temperature vs chlorine.
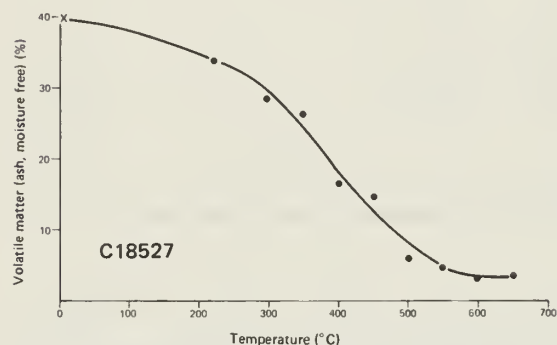
FIGURE 9. Temperature vs percentage of volatile matter (ash, moisture free).
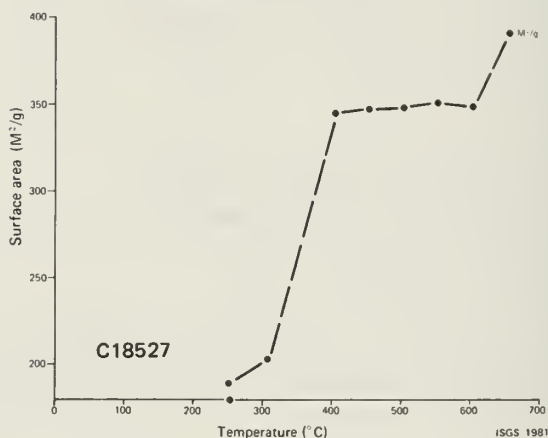
FIGURE 10. Temperature vs surface area.

what different (fig. 10). The internal surface area rises rapidly from 300-400° C and then levels off until 600°C, where it again rises. There is no plateau near 350°C, as occurred in the high-sulfur coal (figs. 6,10). The plot of chlorine (fig. 8) shows a rapid loss below 400°C and then a much slower rate of release or a leveling off.

Results for these two coals (figs. 1-10) were the basis for selecting the two operating temperatures used in this study. The lower temperature (450°C) is that below which most of the volatiles and sulfur are lost and the char probably has a reduced internal surface area. The higher temperature (600-700°C) is the point just before the coal structure begins to break down totally after most of the sulfur, chlorine, and volatile matter has been lost. Near this temperature the chars exhibit their highest internal surface area.

Results of elemental analysis of char from five coals

Results are grouped according to starting coals; in most cases, results from all three charring units are reported. Temperature, weight of starting coal, weight of residue, and percent recovery (weight of residue/weight of starting coal) are given in the char results data section (p. 17). The percent recovery is generally much the same for the same operating temperature and the same coal despite the use of three different charring units.

The char results section gives results of the analysis of chars from the five coals studied. Analysis of the raw coal was included when available. All

the coals used in the RHS, DK, and CK runs were splits of the same original sample listed in table 1. A single method was used for the analysis of a particular element through a given experiment so that results can be easily compared. All char values are calculated to the dry, whole-coal basis.

To be considered significant, losses for particular elements relative to the raw coal must exceed analytical uncertainties and errors due to the heterogeneous nature of coal. Apparent increases in the concentration of certain elements in the char relative to the raw coal may have resulted from contamination during the charring or subsequent handling or from limitations of the analytical method.

Composition of trapped volatile fraction from the five coals

Direct analysis of condensed volatile products from the pyrolysis systems was difficult. The condensate was a tar-like material that was difficult to process without risk of contamination or loss, and the concentrations of many elements were so low that they were at or just below detection limits.

The cold trapping system most successful with these five coals was that used on the RHS unit (fig. 2). The cold trap consists of two connecting water-jacketed, large-bore glass columns packed with small glass beads to break up the gas flow. This column contains a 50:50 mixture of THF and dimethoxy-propane to dissolve the organics. The dimethoxypropane also converts the water produced during the charring process to acetone and methanol which can be removed easily with the solvent. The thick condensed tars are collected by evaporation of the solvent in a rotary evaporator. The analytical results of the volatile elements trapped during the pyrolysis of three of the coals are shown in table 4.

TABLE 4. ANALYSIS OF TRAPPED VOLATILE FRACTION.

Analysis Number	C20301	C20322	C20318	C20320	C20399
Starting Coal	C18571	C18571	C18857	C18857	C18440
Apparatus	RHS	RHS	RHS	RHS	RHS
Temp °C	450	600	450	600	1000
% Trapped	13.8	12.7	12.9	15.9	2.8
Fe	5.2	0.9	0.9	0.6	0.2
K	0.7	1.0	0.5	0.7	0.05
Na	1.2	1.3	0.8	1.4	0.8
As	0.03	0.04	0.3	0.05	0.08
Br	0.4	0.8	0.8	1.1	0.3
Co	0.001	<0.004	0.003	0.001	0.001
Cr	0.08	0.05	0.13	0.05	0.01
Ga	<.1	0.01	0.012	0.01	<0.01
Hf	<.01	<0.01	<0.1	<0.1	<0.01
La	0.001	<0.01	<0.01	0.003	<0.001
Ni	<1	<1	<1	<1	<1
Rb	<.5	<.5	<1	<1	<1
Sb	0.014	0.06	0.02	0.02	0.003
Sc	0.0002	0.0001	0.0001	0.0001	<0.001
Se	0.21	0.22	0.15	0.25	0.11
Sm	<.1	<.1	0.0002	<0.01	<0.001
Th	<.1	<.1	<0.1	<0.1	<0.01
Yb	0.001	.001	<0.001	<0.01	<0.01
Zn	0.3	0.2	0.3	0.5	

* Values corrected to dry whole coal basis. All values expressed in PPM.

Mass balance calculations were made by using analytical results of char, trapped volatile material, and coal. However, the very low concentrations and incomplete trapping of all volatile trace elements made this type of calculation generally unreliable for many of the elements present in the coal; for this reason, these calculations are not presented in this paper.

DISCUSSION

Chlorine, Br, Se, Pb, As, Co, I, Cu, Sb, and U were all mobile to some extent in at least one of the five coals studied.

Starting coals	Mobile elements
C18185	Cl, Br, Cu, Pb, Se
C18440	As*, Br, Se
C18571	Cl, Br, Co*, I*, Pb(?), Se*
C18848	Cl, Br, Se(?), U*
C18857	Cl, Br, Cu(?), I*, Pb(?), Sb(?), Se*

(*) Elements in which only results from one pyrolysis unit showed loss.
(?) Elements in which the assignment of mobility was very near the experimental uncertainty.

An element was considered to be mobile if the difference between its concentration in the starting coal and in the char, on a normalized basis, was greater than the experimental uncertainty for that particular element. A greater than 20 percent change in concentration was required for the change to be considered significant. An element was designated questionable when doubt existed about its mobility.

Chlorine and Br are the only elements showing losses in all the coals for which they were determined. Lead and Se are generally lost but, in some cases, the loss is only partial and near the order of experimental uncertainty. Arsenic, Co, Cu, I, Sb, and U are partly mobile in some of the coals studied.

The results of previous researchers on elements reported to be volatile in coal (summarized here) generally corroborate the findings of this study, despite the lower pyrolysis temperatures used in this study. (See references section for source of data.)

    Klein: Br, Cd, Cl, Cu, Ga, Hg, Mo, Pb, Sb, Se, Zn
    Davidson: As, Cd, Cr, Ni, Pb, Sb, Se, Tl, Zn
    Kaakinen: As, Cu, Hg, Mo, Sb, Zn, Se, Pb
    Cole: As, Cd, Ga, Mo, Pb, Sb, Se, W, Zn
    Block: Br, Cl, Hg, Sb, As, I, Se
    Ting: As, Cl, Se
    Bertine: As, Bi, Cd, Hg, Pb, Sb, Sn, Tl, Zn
    Ruch: Br, Hg, Sb

Zinc, Ga, Mo, Ni, and Cr, which have been reported in other studies to be volatile, were generally immobile in our study. The volatilities of Bi, Cd, Hg, Sn, and Tl were not determined in this work.

Element concentrations in the trapped volatile fractions confirm conclusions based on char losses. Bromine and Se are present in relatively high concentrations. Arsenic, Cr, Sb, and Zn are occasionally present in trace concentrations, indicating their partial volatility at temperatures of 450-700°C.

Using results from previous work on the organic association of trace elements in the same coals studied in this report, Kuhn et al. (1980) observed retention factors for elements in mineral-matter-free fractions (table 5). Because of the number of uncertainties involved in the determination of retention factors (i.e., degree of organic association, including possible contamination by the acid or incomplete removal of small quantities of finely disseminated mineral matter), the results show trends only. For Br, all five coals have a retention of more than 60 percent (a very high organic association). Results for Se, Cu, Sb, U, Co, As, and Pb show mixed or inconclusive associations; however, more important is the range of association observed for particular elements. For example, Se has retention percentages ranging from 5 to 50, but the Se mobility exhibits no relationship to these percentages. If organically associated elements are assumed to be relatively mobile, then such a relationship ought to be evident. In contrast, Cu showed the highest mobility in C16173; this sample also had the highest retention factor or organic association for Cu. In C18848, however, Co showed a high retention factor or organic association but no clear mobility. Arsenic was mobile in C18440, which also had a high organic association, but Sb was immobile in coal samples C18185, C18440, and C18848, all three of which had high organic affinities for Sb. Thus, the relationship between volatility and elemental association with the organic fraction of coal is unclear. Also, because of the very low concentrations of many trace elements in coal, char, and especially in mineral-matter-free coal, cumulative analytical uncertainties make it very difficult to relate the form of an element to its mobility. At best, relationships reported here are semiquantitative.

TABLE 5. PERCENT RETENTIONS[†] FOUND IN MINERAL-MATTER-FREE COAL. Kuhn et al. (1980)

	C18185	C18440	C18571	C18848	C18857
As	22	50	--*	--	--
Br	67	>100	65	68	80
Cr	43	9	10	54	21
Co	17	12	9	55	7
Cu	54	16	--	17	--
Ga	22	9	17	1	22
Pb	--*	--	--	--	--
Sb	47	66	--	48	--
Se	13	50	12	17	5
U	12	30	7	33	--
Zn	--*	--	--	--	--
La	25	7	16	16	9
Ce	21	7	9	12	12
Sm	50	18	32	2	24
Eu	29	27	21	21	25
Yb	27	16	19	31	37
Th	35	22	18	--	29

*No retention fraction determined because the concentration in the mineral-matter-free coal was below the detection limit.
[†]Concentration in the mineral-matter-free coal divided by concentrations in the raw coal.

Results from tables 2 and 3 indicate that an important factor in the movement of elements is the changing internal surface area or pore size of coal as it is heated. Elements that are found adsorbed on the pore surface should have a greater opportunity for volatilization than those which are contained within the coal structure. (The latter, indeed, may be organically combined.) When the coal structure breaks down into a slag at high temperatures, such as occurs in power plants, it is unlikely that many elements escape from it. The kinetic question of how fast the volatile fraction escapes from the coal structure needs to be considered. A volatile species, because of its placement in small pores, may be trapped within the coal because of plugging of pores by charring volatile organics and thus may require a higher temperature to mobilize it than would usually be needed. The thickness of the bed, the particle size of the coal being charred, and the disposition of volatile products all could influence observed volatilities. Apparent element mobility may thus be significantly different for different coals, regardless of element association.

The formation of volatile chloride compounds at relatively low temperatures suggests that chlorine occurs in coal in a more volatile form than sodium chloride. Gluskoter and Rees (1964) proposed that chlorine was in an inorganic form in coal but that during combustion, chlorine reacts with SO_2 or SO_3 and is liberated. This same mechanism could also affect the mobility of certain trace elements. The formation of various halides or sulfides from the reaction of naturally occurring compounds containing chlorine or sulfur in coal could have the effect of increasing an element's volatility. Thus, an element could be much more volatile in its new form than it was in the original coal compound, regardless of the initial association of the elements.

Consequently, it is difficult to predict element mobility from organic associations as measured here. Results of organic affinity studies give indirect evidence of an element's association, but the application of an organic affinity index to the prediction of volatilities achieved only fair success. The change in the physical structure of coal (i.e., in the internal surface area) with increasing temperature no doubt affects the ability of volatile compounds to escape. The point at which the coal structure totally breaks down is also the point at which additional losses of most elements would not be expected.

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CONDITIONS AND RECOVERIES FOR CHARRING EXPERIMENTS

Analysis Number	Apparatus	Temp (°C)	Time of Char (min)	Dry Weight of Charge (gr)	Dry Weight of Residue (gr)	% Recovery
Starting Coal - C18185						
C20609	RHS	450	200	100.0	66.7	66.7
C20608	RHS	600	200	100.0	59.8	59.8
C20595	CWK	450	45	1353	847	62.6
C20594	CWK	600	15	1384	887	64.0
C19931	DK3	450	80	31.6^X	22.7^X	72.0
C19932	DK3	700	80	36.4^X	22.6^X	62.1
C19776*	DK2	450	80	10.7	7.8	73.0
C19871*	DK2	700	90	10.2	6.4	62.9
C19666*	DK1	450	110	10.6	8.0	75.4
C19667*	DK1	700	120	10.7	7.0	65.1
Starting Coal - C18440						
C20612	CWK	450	45	573	346	60.4
C20611	CWK	600	15	574	355	61.8
C20607	RHS	450	200	100	63.3	63.3
C20606	RHS	600	200	100	57.9	57.9
C20400	RHS	1000	125	77.6	43.2	55.7
C19952	DK3	400	80	30.2^X	19.4^X	64.1
C19953	DK3	700	75	25.3^X	20.9^X	82.7
C19773*	DK2	400	75	9.87	6.52	66.1
C19872*	DK2	700	80	10.6	5.9	55.9
C19663*	DK1	400	110	10.1	7.0	69.2
C19664*	DK1	700	120	10.8	6.3	58.0
Starting Coal - C18571						
C20496*	RHS	450	200	100.0	72.8	72.8
C20494*	RHS	600	240	100.0	67.3	67.3
C20300	RHS	450	200	100.0	71.5	71.5
C20321	RHS	600	195	100.0	62.2	62.2
C20298*	CWK	450	45	970	669	68.9
C20299*	CWK	600	15	913	593	64.9
C19943	DK3	450	80	39.2^X	27.9^X	71.1
C19944	DK3	700	80	41.6^X	27.1^X	65.5
C19668*	DK1	450	90	10.11	7.36	72.8
C19683*	DK1	700	120	11.02	7.15	64.9
Starting Coal - C18848						
C20605	RHS	450	200	100.0	92.2	92.2
C20604	RHS	600	200	100.0	88.3	88.3
C20579	CWK	450	80	1388	1310	94.4
C20580	CWK	600	15	1400	1192	85.1
C19949	DK3	450	80	28^X	25^X	89.4
C19950	DK3	700	80	25.3^X	20.9^X	82.3
C19774*	DK2	450	80	10.28	9.32	90.1
C19875*	DK2	700	80	10.26	8.52	83.0
C19644*	DK1	450	110	10.30	9.59	93.1
C19645*	DK1	700	100	9.73	8.21	84.4
Starting Coal - C18857						
C20317	RHS	450	200	100.0	68.9	68.9
C20319	RHS	600	195	100.0	62.6	62.6
C19934	DK3	450	60	51.8^X	35.4^X	68.3
C19935	DK3	700	60	60.0^X	36.1^X	60.2
C19775*	DK2	450	80	10.94	7.42	67.8
C19874*	DK2	700	80	10.59	6.96	65.7
C19679*	DK1	450	120	9.91	7.10	71.6
C19680*	DK1	700	120	10.18	6.33	62.2

* Samples where no elemental data are presented.

^{X} Sample represents the combination of three trials.

LAB.NO.	GEOL.NO.	AL	CA	CL	FE	K	MG	NA	SI	TI
C20586	110 RHS	0.77%	4.38%	67 ppm	1.41%	0.14%	0.07%	260 ppm	2.2 %	0.05%
C20609	450 RHS	0.78%	2.89%	59 ppm	1.41%	0.12%	0.08%	230 ppm	2.2 %	0.05%
C20608	600 RHS				1.3 %	0.12%		230 ppm		
C20595	450 CWK				1.2 %	0.11%		210 ppm		
C20594	600 CWK				1.4 %	0.13%		240 ppm		
C19933	110 DK3	0.82%	1.16%	200 ppm	1.23%	0.11%	0.06%	375 ppm	2.22%	0.05%
C19931	450 DK3	0.88%	1.42%	70 ppm	1.35%	0.11%	0.08%	374 ppm	2.37%	0.05%
C19932	700 DK3	0.79%	1.83%	60 ppm	1.37%	0.12%	0.09%	366 ppm	2.37%	0.04%
C20610	110 RHS	1.00%	13.0 %	60 ppm	0.23%	300 ppm	0.20%	3200 ppm	1.72%	0.06%
C20607	450 RHS	1.00%	11.7 %	60 ppm	0.21%	312 ppm	0.20%	3040 ppm	1.87%	0.06%
C20606	600 RHS				0.3 %	370 ppm		3000 ppm		
C20400	1000 RHS				0.3 %	220 ppm		2700 ppm		
C20612	450 CWK				0.19%	204 ppm		2800 ppm		
C20611	600 CWK				0.22%	300 ppm		2900 ppm		
C19954	110 DK3	0.99%	2.52%	100 ppm	0.24%	218 ppm	0.26%	3340 ppm	1.66%	0.07%
C19952	400 DK3	0.81%	2.45%	100 ppm	0.24%	125 ppm	0.24%	3300 ppm	1.26%	0.06%
C19953	700 DK3	0.80%	2.48%	100 ppm	0.24%	154 ppm	0.26%	3200 ppm	1.39%	0.06%
C20297	110 RHS	1.73%	0.48%	300 ppm	2.73%	0.20%		520 ppm	3.95%	0.11%
C20300	450 RHS	1.70%	0.52%	70 ppm	1.80%	0.20%		515 ppm	4.01%	0.06%
C20321	600 RHS	1.64%	0.62%	60 ppm	1.40%	0.16%		480 ppm	3.92%	0.06%
C19945	110 DK3	1.19%	0.61%	1900 ppm	1.95%	0.16%	0.07%	1390 ppm	2.5 %	0.06%
C19943	450 DK3	1.00%	0.45%	800 ppm	2.10%	0.16%	0.04%	1350 ppm	2.2 %	0.06%
C19944	700 DK3	1.07%	0.43%	200 ppm	1.98%	0.17%	0.04%	1400 ppm	2.2 %	0.06%
C20498	110 RHS	5.67%	0.16%	90 ppm	1.16%	1.21%	0.09%	1400 ppm	10.2 %	0.19%
C20605	450 RHS	5.46%	0.16%	90 ppm	1.02%	1.22%	0.11%	1400 ppm	10.1 %	0.18%
C20604	600 RHS	3.69%	0.17%	90 ppm	1.08%	1.24%	0.09%	1300 ppm	8.43%	0.19%
C20579	450 CWK				0.86%	1.14%		1300 ppm		
C20580	600 CWK				0.96%	1.14%		1300 ppm		
C19951	110 DK3	2.12%	0.29%	200 ppm	0.42%	0.26%	0.04%	400 ppm	2.79%	0.16%
C19949	450 DK3	2.01%	0.26%	90 ppm	0.47%	0.29%	0.06%	400 ppm	2.46%	0.15%
C19950	700 DK3	2.04%	0.28%	80 ppm	0.43%	0.24%	0.04%	400 ppm	2.43%	0.14%
C20239	110 RHS	1.62%	0.15%	700 ppm	1.9 %	0.16%		774 ppm	2.43%	0.09%
C20317	450 RHS	1.62%	0.18%	100 ppm	2.5 %	0.14%		690 ppm	2.47%	0.05%
C20319	600 RHS	1.58%	0.14%	60 ppm	2.4 %	0.15%		700 ppm	2.48%	0.06%
C19936	110 DK3	1.05%	0.33%	900 ppm	1.8 %	0.13%	0.05%	780 ppm	2.49%	0.06%
C19934	450 DK3	0.92%	0.33%	200 ppm	1.9 %	0.10%	0.06%	680 ppm	2.18%	0.05%
C19935	700 DK3	0.81%	0.37%	100 ppm	1.8 %	0.10%	0.04%	660 ppm	2.25%	0.05%

LAB.NO.	GEOL.NO.	S	H2O-	VOLAT	AS (PPM)	BA (PPM)	BR (PPM)	CE (PPM)	CO (PPM)	CR (PPM)
C20586	110 RHS	3.29%	3.1%	39.1%	11	25	2	5	2.3	12
C20609	450 RHS	2.25%	0.5%	13.2%	10	31	1.5	4	2.2	11
C20608	600 RHS	1.80%	0.7%	5.6%	10	27	1.1	4	2.0	11
C20595	450 CWK	2.26%	0.5%	12.4%	10	25	1.2	4	1.9	10
C20594	600 CWK	2.34%	0.4%	5.9%	11		1.0	5	2.2	13
C19933	110 DK3				5.6	46	2.2	4.1	3.1	15
C19931	450 DK3				4.8	46	1.6	4.6	3.2	17
C19932	700 DK3				4.8	51	1.2	5.3	2.4	16
C20610	110 RHS	0.53%	9.4%	40.6%	2.3	250	2.4	8.5	0.9	2.9
C20607	450 RHS	0.27%	0.8%	12.6%	1.9	234	1.9	7.9	0.8	2.8
C20606	600 RHS	0.28%	1.0%	6.2%	1.9	260	1.9	8.4	0.9	3.6
C20400	1000 RHS				2.1	262	2.2	8.9	1.1	2.6
C20612	450 CWK	0.31%	2.2%	16.1%	1.9	217	1.9	7.4	0.6	3.0
C20611	600 CWK	0.30%	2.0%	12.9%	2.1	230	1.5	7.7	0.8	2.5
C19954	110 DK3				2.5	400	2.8	9.0	1.2	2.6
C19952	400 DK3				1.6	400	1.7	8.4	1.4	2.8
C19953	700 DK3				1.6	410	1.9	8.7	1.2	2.6
C20297	110 RHS	3.57%	3.0%	37.5%	1.9	54	2.3	12	7.4	18
C20300	450 RHS	1.69%	0.50%		1.5	54	1.8	10	5.1	21
C20321	600 RHS				1.4	49	1.4	7	5.0	22
C19945	110 DK3				2.7	56	11	9	6.4	20
C19943	450 DK3				2.0	61	9	9	6.5	20
C19944	700 DK3				2.6	61	4	12	6.2	21
C20498	110 RHS	0.30%	0.1%	14.4%	7.8	556	1.8	58	11	73
C20605	450 RHS	0.31%	0.4%	6.8%	6.5	590	1.1	55	10	66
C20604	600 RHS	0.32%	0.6%	4.0%	6.8	594	1.1	56	10	67
C20579	450 CWK	0.35%	0.7%	11.0%	6.7	544	1.5	51	9.4	62
C20580	600 CWK	0.29%	0.5%	6.6%	5.9	520	1.4	51	9.4	62
C19951	110 DK3				4.1	230	3.4	31	17	24
C19949	450 DK3				9.7	234	2.1	29	16	25
C19950	700 DK3				3.0	233	1.4	31	16	26
C20239	110 RHS	3.27%	4.3%	39	1.6	53	3.6	12	2.8	13
C20317	450 RHS	3.00%	0.7%		1.5	56	2.7	10	2.5	14
C20319	600 RHS	2.62%	0.4%		1.6	54	1.9	9	2.5	13
C19936	110 DK3				1.3	52	4.1	6	4.7	20
C19934	450 DK3				1.3	52	2.5	6	4.5	18
C19935	700 DK3				1.3	51	2.1	7	4.2	16

CHAR ANALYSIS DATA

LAB.NO.	GEOL.NO.	CS (PPM)	CU (PPM)	EU (PPM)	GA (PPM)	HF (PPM)	I (PPM)	LA (PPM)	LU (PPM)	MN (PPM)
C20586	110 RHS	0.9		0.09	2.5	0.3		2.3	0.08	
C20609	450 RHS	0.8		0.07	2.2	0.3		2.5	0.17	
C20608	600 RHS	0.6		0.08	2.3	0.4		2.3	0.08	
C20595	450 CWK	0.7		0.07	2.1	0.3	3.4	2.2	0.14	
C20594	600 CWK	0.8		0.09	2.2	0.4	3.0	2.5	0.10	
C19933	110 DK3	0.8	18	0.10	2.5	0.4	2.5	2.9	0.08	200
C19931	450 DK3	0.8	11	0.09	2.3	0.5	2.6	2.6	0.06	190
C19932	700 DK3	0.9	7	0.10	2.4	0.5	2.8	2.6	0.06	170
C20610	110 RHS	0.1		0.11	3.2	0.6	1.6	5.6	0.05	
C20607	450 RHS	0.06		0.10	2.8	0.7	2.4	5.4	0.05	
C20606	600 RHS	0.2		0.11	2.8	0.7	2.3	6.0	0.06	
C20400	1000 RHS	0.08		0.11	2.9	0.14	1.9	5.8	0.06	
C20612	450 CWK	0.12		0.08	1.9	0.6	2.1	5.2	0.09	
C20611	600 CWK	0.10		0.10	3.6	0.6	1.8	5.3	0.04	
C19954	110 DK3	0.06	3.6	0.15	2.8	0.9	4.3	7.3	0.05	71
C19952	400 DK3	0.06	3.3	0.11	2.9	0.8	3.9	6.1	0.05	68
C19953	700 DK3	0.07	2.2	0.17	2.3	1.0	3.7	5.6	0.05	67
C20297	110 RHS	1.3		0.2	3.2	0.6	1.6	5.0	0.16	
C20300	450 RHS	1.2		0.2	3.3	0.7	0.7	5.0	0.14	
C20321	600 RHS	1.0		0.2	3.3	0.5	0.9	4.3	0.09	
C19945	110 DK3	1.2	9.4	0.3	4.0	0.5	3.0	6.1	0.09	64
C19943	450 DK3	1.3	8.5	0.3	3.6	0.5	3.3	6.6	0.08	60
C19944	700 DK3	1.4	8.9	0.3	4.0	0.6	2.7	6.4	0.08	58
C20498	450 RHS	10		1.0	17	3.2	3.7	31	0.5	68
C20605	600 RHS	11		0.9	16	3.0	6.3	29	0.4	60
C20604	600 RHS	10		0.9	16	3	6.2	29	0.4	64
C20579	450 CWK	9.4		0.8	16	3	6.1	29	0.4	62
C20580	600 CWK	9.4		0.9	15	2.8	5.6	28	0.5	75
C19951	110 DK3	2.5	17.7	0.6	9.5	1.5	3.4	19	0.15	36
C19949	450 DK3	2.8	17.9	0.5	8.5	1.3	3.2	19	0.15	45
C19950	700 DK3	2.8	17.3	0.6	8.7	1.4	3.0	18	0.16	36
C20239	110 RHS	1.2		0.18	3.1	0.4	1.9	5.4	0.14	34
C20317	450 RHS	0.8		0.21	2.6	0.5	0.9	4.8	0.11	
C20319	600 RHS	0.7		0.19	2.6	0.5	0.7	5.3	0.09	
C19936	110 DK3	1.2	7.8	0.17	7.6	0.5	2.4	3.6	0.08	43
C19934	450 DK3	1.2	7.0	0.16	7.6	0.5	1.6	3.8	0.08	46
C19935	700 DK3	1.1	6.7	0.15	6.8	0.6	1.5	3.5	0.05	43

CHAR ANALYSIS DATA

LAB.NO.	GEOL.NO.	NI (PPM)	F (PPM)	PB (PPM)	RB (PPM)	SB (PPM)	SC (PPM)	SE (PPM)	SM (PPM)	SR (PPM)
C20586	110 RHS	<5			13	1.7	1.7	2.6	0.5	11
C20609	450 RHS	<5	40		11	1.5	1.5	1.9	0.4	12
C20608	600 RHS	<6	36		11	1.5	1.5	2.0	0.4	12
C20595	450 CWK	<6	47		9	1.4	1.4	1.6	0.4	9
C20594	600 CWK	<4	32		11	1.7	1.7	2.1	0.6	
C19933	110 DK3	5.6	24	31	16	1.5	1.7	3.6	0.5	26
C19931	450 DK3	5.7		5.5	24	1.4	1.8	2.7	0.5	25
C19932	700 DK3	5.5		5.2	20	1.2	1.8	2.4	0.5	26
C20610	110 RHS	<2	54		<5	0.8	1.3	1.0	0.5	190
C20607	450 RHS	<2	50		<5	0.8	1.2	0.6	0.7	186
C20606	600 RHS	<2			<5	1.0	1.3	0.6	0.6	165
C20400	1000 RHS	<8			<5	0.8	1.1	1.0	0.6	200
C20612	450 CWK	<5			<5	0.7	1.2	0.8	0.4	162
C20611	600 CWK	<5			<5		1.6	0.6		168
C19954	110 DK3	1.5	52	7.9	<10	1.0	1.3	1.4	0.6	254
C19952	400 DK3	1.2	37	7.4	<10		1.3	1.0	0.6	230
C19953	700 DK3	1.5	33	5.8	<6	1.3	1.3	1.0	0.6	240
C20297	110 RHS	14			21	0.3	3	2.3	1.0	17
C20300	450 RHS	21			19	0.3	3	2.2	1.0	18
C20321	600 RHS	16			14	<1	2.5	1.6	1.0	18
C19945	110 DK3	17	49	8.5	23	0.6	2.5	2.9	1.4	31
C19943	450 DK3	16	34	7.1	26	0.9	2.5	2.5	1.5	36
C19944	700 DK3	13	34	6.6	25		2.7	2.1	1.4	36
C20498	110 RHS	30	70		90	1.2	15	2.2	4.9	71
C20605	450 RHS	34	70		87	1.0	14	2.0	5.0	74
C20604	600 RHS	36	73		91	1.3	13	1.7	4.9	72
C20579	450 CWK	40			83	1.1	12	1.8	4.5	70
C20580	600 CWK	58			86		13	1.4	4.8	66
C19951	110 DK3	7	52	9.7	30	1.6	7.0	2.3	2.9	73
C19949	450 DK3	19	48	10.4	37	2.0	6.3	2.9	2.8	69
C19950	700 DK3	14	45	9.7	31	1.6	6.8	2.9	3.1	73
C20239	110 RHS		24		13	0.5	2.4	2.3	1.0	24
C20317	450 RHS		75		16	0.3	2.1	1.9	1.0	22
C20319	600 RHS		70		11	0.4	1.9	1.7	1.0	22
C19936	110 DK3	7.9	41	6.9	23	0.7	2.2	3.0	0.7	29
C19934	450 DK3	7.3	29	5.5	24	0.5	2.2	2.3	0.7	26
C19935	700 DK3	7.5	25	5.2	20	0.5	2.0	1.7	0.6	27

LAB.NO.	GEOL.NO.	TA	TH	U	W	YB	ZN
C20586	110 RHS	0.10 PPM	1.3 PPM	0.5 PPM	<0.3 PPM	0.3 PPM	1300 PPM
C20609	450 RHS	0.10 PPM	1.1 PPM	0.5 PPM	0.2 PPM	0.3 PPM	1000 PPM
C20608	600 RHS	0.07 PPM	1.1 PPM	0.5 PPM	0.2 PPM	0.2 PPM	1300 PPM
C20595	450 CWK	0.06 PPM	1.0 PPM	0.5 PPM	0.2 PPM	0.3 PPM	1200 PPM
C20594	600 CWK	0.10 PPM	1.1 PPM	0.7 PPM	0.15 PPM	0.3 PPM	1200 PPM
C19933	110 DK3	0.10 PPM	1.2 PPM	2.9 PPM	0.15 PPM	0.3 PPM	1250 PPM
C19931	450 DK3	0.12 PPM	1.3 PPM	2.8 PPM	0.20 PPM	0.3 PPM	1500 PPM
C19932	700 DK3	0.17 PPM	1.3 PPM	2.7 PPM		0.3 PPM	1700 PPM
C20610	110 RHS	0.18 PPM	2.7 PPM	<0.9 PPM	1.4 PPM	0.3 PPM	<10 PPM
C20607	450 RHS	0.16 PPM	2.5 PPM	<0.7 PPM	1.3 PPM	0.3 PPM	4 PPM
C20606	600 RHS	0.17 PPM	2.6 PPM	<0.7 PPM	1.0 PPM	0.3 PPM	6 PPM
C20400	1000 RHS	0.20 PPM	2.8 PPM	<0.8 PPM	1.1 PPM	0.4 PPM	<24 PPM
C20612	450 CWK	0.16 PPM	2.3 PPM	<0.7 PPM	1.0 PPM	0.3 PPM	29 PPM
C20611	600 CWK	0.17 PPM	2.3 PPM	<0.5 PPM	0.8 PPM	0.3 PPM	66 PPM
C19954	110 DK3	0.17 PPM	2.7 PPM	1.0 PPM		0.4 PPM	3 PPM
C19952	400 DK3	0.18 PPM	2.6 PPM			0.2 PPM	2 PPM
C19953	700 DK3	0.17 PPM	2.7 PPM	0.8 PPM		0.2 PPM	1 PPM
C20297	110 RHS	0.15 PPM	2.0 PPM	0.4 PPM	0.3 PPM	0.7 PPM	32 PPM
C20300	450 RHS	0.14 PPM	2.1 PPM	0.7 PPM	0.3 PPM	0.6 PPM	56 PPM
C20321	600 RHS	0.14 PPM	1.6 PPM	0.5 PPM	0.3 PPM	0.5 PPM	62 PPM
C19945	110 DK3	0.14 PPM	1.8 PPM	1.0 PPM	1.1 PPM	0.4 PPM	27 PPM
C19943	450 DK3	0.12 PPM	1.7 PPM	1.6 PPM	<1 PPM	0.4 PPM	46 PPM
C19944	700 DK3	0.14 PPM	2.0 PPM	2.7 PPM	<1 PPM	0.4 PPM	30 PPM
C20498	110 RHS	0.7 PPM	10 PPM	2.4 PPM	1.2 PPM	2.6 PPM	53 PPM
C20605	450 RHS	0.7 PPM	10 PPM	1.0 PPM	1.0 PPM	2.1 PPM	60 PPM
C20604	600 RHS	0.7 PPM	10 PPM	1.0 PPM	1.0 PPM	2.0 PPM	66 PPM
C20579	450 CWK	0.6 PPM	9.4 PPM	3.0 PPM	1.0 PPM	2 PPM	67 PPM
C20580	600 CWK	0.6 PPM	9.4 PPM	2.8 PPM	0.9 PPM	2.0 PPM	150 PPM
C19951	110 DK3	0.3 PPM	4.9 PPM	2.2 PPM	0.6 PPM	1.2 PPM	20 PPM
C19949	450 DK3	0.3 PPM	4.2 PPM	1.8 PPM	0.8 PPM	0.8 PPM	11 PPM
C19950	700 DK3	0.3 PPM	4.5 PPM	2.2 PPM	0.6 PPM	1.3 PPM	17 PPM
C20239	110 RHS	0.11 PPM	1.7 PPM	<1 PPM	0.3 PPM	0.6 PPM	21 PPM
C20317	450 RHS	0.11 PPM	1.4 PPM			0.6 PPM	27 PPM
C20319	600 RHS	0.15 PPM	1.3 PPM			0.6 PPM	10 PPM
C19936	110 DK3	0.11 PPM	1.5 PPM	<1 PPM	0.3 PPM	0.3 PPM	27 PPM
C19934	450 DK3	0.12 PPM	1.5 PPM		0.3 PPM	0.3 PPM	21 PPM
C19935	700 DK3	0.14 PPM	1.5 PPM		0.3 PPM	0.3 PPM	22 PPM

PART II. FEASIBILITY OF A GRAPHITE TRAPPING SYSTEM

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In Part I of this publication, it was reported that coal from the Herrin
(No. 6) Coal Member (C18857 in table 1) was coked in a modified Parr
Pressure Reaction Apparatus and the resulting oils, tars, and gases were
swept from the reaction apparatus with nitrogen (a distance of 40 cm). The
volatile products were collected in a baffled trap containing tetrahydrofuran
and dimethoxypropane. The dimethoxypropane was used to scavenge the water
produced during the coking process and to assure a dry sample after
evaporation. The collected tar was analyzed for volatile elements.
Qualitative results of this analysis are shown in table A.

The formation of intercalation compounds of graphite has been investigated
by other researchers (1-9); however, the intercalation or sorption of metal
salts by graphite has not been used as a method to determine which elements
will migrate from the coal matrix during coking. To improve the detection
of trapped volatile inorganic species, we have developed a method in which
a coal-graphite mixture is charred and then separated into char and graphite
components. Analysis of the graphite fraction has shown which elements were
intercalated or sorbed by the graphite. Elements that had been shown by
others to be mobile during coal combustion (page 12, main text) were of
particular interest. A qualitative summary of those results is included in
in table A.

EXPERIMENTAL PROCEDURES

The new method differs from the others in that: (1) graphite is used as a
trap for migrating inorganic compounds, and (2) coal and graphite are
intimately mixed, migration distances are short, and losses caused by
inefficient transport are minimized.

We used two samples from the Springfield (No. 5) Coal Member (C21555 and
C21554). Both samples were unwashed (raw) coal, which had been crushed
carefully in a manner that preserved approximately 90 percent of the coal
in 20 x 50 mesh (U.S. Standard Sieves) samples. The samples were then
preheated at 170°C for a period of 20 hours to prevent agglomeration during
the coking process.

Spectral grade graphite (National Sp-2X) was screened to give a <100 mesh
sample. Six grams of the 20 x 50 mesh sample and 2 g of the <100 mesh
graphite were mixed thoroughly and heated at 600°C under a purge
(200 cm^3/min) of nitrogen for a period of 2 hours in a quartz combustion
tube (9 mm). After heating, the mixtures were separated using a 100 mesh
(U.S.) screen. The process was repeated two additional times, using the
same graphite and a total of 18 g of coal.

TABLE A. ELEMENTS FOUND TO BE MOBILE.

	Graphite Traps			Studies Referred To				
Elements found	C21555 Springfield (No. 5) Coal	C21554 Springfield (No. 5) Coal	C18857 Herrin (No. 6) Coal Liquid trap	Klein et al. (1)	Davidson et al. (2)	Kaakinen et al. (3)	Coles et al. (4)	Block and Dams (5)
Ag	X	X						
As	X	X		X	X	X	X	X
Br	X	X	X	X				X
Cd	X	X		X	X		X	
Cl	ND	ND	X	X				X
Co	X	X						
Cr	X	X						
Cu	X	X	X	X	X	X		
Eu	X	X						
Fe	X	X						
Ga	X	X		X			X	
Hf	X	X						
Hg	ND	ND		X		X		X
I	X	X	X					X
K	X	X						
La	X	X						
Mo	X			X		X	X	
Na	X	X						
Ni								
Pb	ND	ND	X	X	X	X	X	
Rb	X	X						
Sb	X	X	X	X	X	X	X	X
Sc	X	X		X	X	X		
Se	X	X	X	X	X	X	X	X
Sm	X	X						
Sn	X	X						
Th	X	X						
Tl					X			
U	X	X						
V	X						X	
W								
Yb	X	X						
Zn	X	X		X	X	X	X	

TABLE B. MOESSBAUER PARAMETERS OF IRON SPECIES FOUND IN GRAPHITE TRAPS

Assignment	Isomer Shift*# (mm/s)	Quadrupole Coupling Constant* (mm/s)	Internal Magnetic Field* (KOe)	Fe (%)
PERRY COUNTY COAL SAMPLE				
Pyrrhotite	0.72(1)	0.09(1)	305(3)	27.7
Pyrrhotite	0.75(1)	0.08(1)	284(3)	20.7
Pyrrhotite	0.73(1)	0.13(1)	266(2)	37.0
Pyrite	0.34(1)	0.67(1)		14.6
GALLATIN COUNTY COAL SAMPLE				
Pyrrhotite	0.75(1)	0.07(1)	314(3)	27.1
Pyrrhotite	0.75(1)	0.09(1)	293(3)	9.5
Pyrrhotite	0.74(1)	0.14(1)	271(2)	28.4
Pyrite	0.23(3)	0.52(2)		35.0

*Error factors in last digit are given in parentheses.
#Shifts reported vs NBS iron foil.

RESULTS

The results of neutron activation, energy dispersive X-ray fluorescence, and optical emission spectrographic analyses of the separated graphite samples (table A) show which elements migrated and were therefore inter-calated or sorbed by the graphite. Twenty-six elements were found in the graphite fraction. Determinations were not made for four elements (Cl, Hg, S, and Pb). These elements are also very likely to be mobile.

The two recovered graphite fractions were analyzed using Moessbauer spectro-scopy, as described previously (10-14). The predominant iron species were pyrrhotite and a species similar to pyrite (table B). The Fe^{+2} illite species, which occurred in the No. 5 Coal (C21555) in a relatively high concentration, was not found in the graphite, indicating that the graphite was not contaminated with a significant amount of the coal char. Optical microscopic examination and X-ray diffraction analysis also detected no residual char as a contaminant in the recovered graphite fraction.

Down-stream, graphite trapping of the trace metals within the process vessel utilized an apparatus similar to that just described for the graphite-coal mixture experiments but with three modifications. In the first modification, the quartz tube was packed with preheated coal and graphite separated 2.0 cm by a quartz wool divider. In addition to the two Springfield (No. 5) coal members (C21555 and C21554) used previously, a Herrin (No. 6) coal member (C18527) was also used. The elements found in this modification of the graphite trap are listed in table C. One disadvantage of this method is that tar produced during the pyrolysis tends to leave a carbon residue on the quartz wool. It was not determined whether any of the elements were sorbed by the carbon on the quartz wool divider.

In the second modification, the quartz tube was packed with fresh Herrin (No. 6) coal (C21556) (12 x 16 mesh- U.S. Screen) separated (0.5 cm) from the graphite by a trace-element-free parafilm. Upon heating at low temperatures, the parafilm melts and distills from the system. The coal then cokes to form a solid cake that fills the tube. The graphite can then be easily separated from the solid cake because it pours freely from the tube. The elements found in the parafilm modification of the graphite trap are shown in table C.

TABLE C. ELEMENTS OBSERVED IN GRAPHITE TRAPS

Element / Seam	Quartz Wool Plug — Preheated Springfield (No. 5) Coal B	Quartz Wool Plug — Preheated Springfield (No. 5) Coal B	Quartz Wool Plug — Preheated Springfield (No. 5) Coal A	Quartz Wool Plug — Preheated Springfield (No. 5) Coal A	Quartz Wool Plug — Preheated C18527 (No. 6) Coal	Quartz Wool Plug — Preheated C18527 (No. 6) Coal	Parafilm Plug — Raw C21556 Herrin (No. 6) Coal	Parafilm Plug — Raw C21556 Herrin (No. 6) Coal	No Plug — Preheated C21556 Herrin (No. 6) Coal	No Plug — Raw C21556 Herrin (No. 6) Coal
Pyrolysis Temp.	600°C	700°C	600°C	700°C	600°C	700°C	700°C	700°C	700°C	700°C
Trap Temp.	600°C	700°C	600°C	700°C	600°C	700°C	700°C	300°C	300°C	300°C
Al	X	X	X	X			X			
As	X	X	X	X	X	X	X	X	X	X
B		X	X	X						
Br	X	X	X	X	X	X	X	X	X	X
Co	X		X	X	X	X	X	X	X	X
Cr	X	X	X				X	X	X	X
Cs		X	X	X						X
Cu	X						X			
Fe	X	X	X	X		X	X	X	X	
K	X	X	X	X		X	X	X		
La	X		X							
Mg	X	X	X	X	X	X	X	X	X	X
Na	X	X	X	X	X	X	X	X	X	X
Ni								X		
Sb	X	X	X	X		X	X	X		X
Sc		X	X	X	X					
Se	X	X	X	X	X	X			X	X
Zn								X		

The third modification contains the fewest obstructions between the graphite and coal, and can be used with raw or preheated coal samples. Two ovens and two quartz tubes are used. One of the quartz tubes that contains the coal is heated at 700°C in the first oven, then slides into the other quartz tube containing the graphite, which is maintained at 300°C by the second oven. The graphite was located 12 cm downstream from the coal. The 300°C temperature was used to help eliminate possible exfoliation of any inter-calated metal salts that may have formed during pyrolysis. After the coking process is complete, the tubes can be easily separated to give coke and graphite fractions. The elements found to be mobile during the pyrolysis of a preheated and a raw Herrin (No. 6) coal member (C21556) using this modification are also shown in table C.

Eighteen elements were found in the graphite traps (table C) and were considered to be mobile. Of these, Al, B, Cs, and Mg were found to be immobile with the graphite-coal mixture method (table A). Chlorine, Hg, S, and Pb, although potentially mobile, were not determined; therefore, they have not been included in the list of mobile elements.

Migration distances were dramatically shortened when the coal-graphite mixture was used instead of the Parr Reactor (designated RHS in the main text). This graphite trap method provided a new, more sensitive assessment of element mobility over short distances. Although 26 elements were found to migrate short distances in the coal-graphite mixture (table A), this should not be construed to mean that all of these elements are volatile and escape the coal matrix during ashing.

Migration distances were lengthened from 0.5 cm (parafilm) to 2.0 cm (quartz wool) and then to 12 cm (no divider was present). Thirteen elements were mobile at 0.5 cm, and 17 elements were found to be mobile at the 2.0 cm distance. When no divider was used (12 cm), the number of elements showing mobility dropped to 11. This compares with a maximum of 10 elements (see table 12, main text) for other trapping systems studied. The decomposition of the parafilm and the distillation of its products probably interferes with the trace element trapping mechanism.

Finally, in the Parr Pressure Reaction Apparatus study of coal C18857, only seven elements were sufficiently mobile to migrate from the coking vessel to the liquid trap (a distance of 40 cm). However, direct analysis of the condensed volatile products from the Parr pyrolysis system was difficult. The condensate was a tar-like material that was difficult to process without the risk of contamination or loss, and the concentrations of trace elements found were close to or below detection limits. Normally a 20 percent change in concentration was required to overcome the experimental uncertainty for the element.

Because the pure graphite is initially free of metals, it gives the mass balance study an error free starting point. This property and the fact that the graphite is easy to handle makes the graphite trap a sensitive indicator of element mobility. Not only does the graphite trap appear to be more sensitive than the other methods; it is also more adaptable for experimentation. Variables such as pyrolysis and trapping temperatures, and, most importantly, migrational distances, can be easily adjusted to meet the conditions of a desired experiment.

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